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During the last grant period, we have used negative ion photoelectron spectroscopy (PES) and ZEKE spectroscopy to probe the spectroscopy and dynamics of negatively-charged and neutral species. Specific areas include (a) ZEKE spectroscopy of diatomic rare gas halides (RgX^-) and clusters of the form Rg_nX^-, (b) PES of $I_2^-(Ar)_n$ and $I_2^-(CO_2)_n$, in which the effects of solvation on a molecular (as opposed to atomic) ion are probed, (c) PES as a probe of neutral radicals and reactive intermediates, specifically I_3, CH_3O, and NCN, and (d) time-resolved studies of excited state dynamics in $I^-(H_2O)_n$ clusters using femtosecond photoelectron spectroscopy (FPES).

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Abstract:

During the last grant period, we have used negative ion photoelectron spectroscopy (PES) and ZEKE spectroscopy to probe the spectroscopy and dynamics of negatively-charged and neutral species. Specific areas include (a) ZEKE spectroscopy of diatomic rare gas halides (RgX^-) and clusters of the for Rg_nX^-, (b) PES of $I_2^-(Ar)_n$ and $I_2^-(CO_2)_n$, in which the effects of solvation on a molecular (as opposed to atomic) ion are probed, (c) PES as a probe of neutral radicals and reactive intermediates, specifically I_3, CH_3O, and NCN, and (d) time-resolved studies of excited state dynamics in $I^-(H_2O)_n$ clusters using femtosecond photoelectron spectroscopy (FPES).

Technical Summary:

(a) ZEKE spectroscopy of diatomic RgX^- species and Rg_nX^- clusters

We have measured ZEKE spectra of the diatomic species $KrBr^-$, $KrCl^-$, $XeBr^-$, XeI^-, and $ArCl^-$.[1-3] In these experiments, the anions are photodetached to access the ground *X* (1/2) and low-lying *I* (3/2) and *II* (1/2) electronic states of the open shell RgX species; the number in parentheses is Ω, the projection of the electronic and spin angular momentum on the internuclear axis, since Hund's case (c) is appropriate here. The *X* and *I* states correlate to the Rg + $X(^2P_{3/2})$ asymptote, whereas the *II* state correlates to the higher-lying Rg + $X(^2P_{1/2})$ asymptote.

The resolution of the spectrometer is as high as 1 c^{-1}, allowing us to observe vibrational transitions between the anion and three neutral electronic states. By fitting the spectra to model potentials, we obtain high quality pair-potentials for the anion and neutral states. The neutral potentials can also be extracted from scattering[4-6] and, in some cases, emission spectroscopy experiments;[7,8] our analysis generally incorporate this earlier work and results in a full set of three high quality neutral potentials. Our anion potentials represent a significant improvement over those obtained from ion mobility measurements,[9-11] the only experimental technique other than ours from which these potentials have been extracted. We find that the ion mobility potentials typically overestimate the RgX^- well depth by 25-50% and underestimate the equilibrium internuclear separation by as much as 1 Å.

We have also measured ZEKE spectra of the larger clusters Rg_nX^-, in order to study in detail the effects of solvation on the anion and neutral halogen atom. Results were obtained for Xe_nI^- clusters with up to 14 Xe atoms[12] and Ar_nCl^- clusters with up to 15 Ar atoms. These experiments yield accurate electron affinities and neutral state splitting as a function of cluster size. Since all the pair potentials within the anion and neutral cluster are well-determined from both our diatomic ZEKE experiments and previous work on Rg_2 potentials, our experiments provide a sensitive probe of many-body effects in the larger clusters. By performing molecular dynamics simulations on the anion and neutral clusters using our pair potentials and successive non-additive terms, we can determine which non-additive terms are needed and their relative importance. Specifically, we find that using pair potentials alone significantly overestimates the electron affinities. The inclusion of induction effects in the anion overcorrects for this, yielding electron affinities that are too low. Much of this overcorrection is removed by including exchange-induced quadrupole interactions in the anion, and very good agreement with experiment is obtained from including additional many-body effects.

The experimental and theoretical work on Xe_nI^- is of particular interest as it shows there is no solvent shell closure at n=12, as had been expected fro mass spectrometry measurements.[13] Instead, our simulations show that the lowest energy structures for n=13 and 14 consist of a single solvent shell around the I^-. Simulations using the pair potentials alone yield a shell-closing at n=12, so it appears that the inclusion of many-body effects changes the geometries of the lowest-energy structures for the n=13 and 14 clusters.

(b) Photoelectron spectroscopy of $I_2^-(Ar)_n$ and $I_2^-(CO_2)_n$ clusters

The work described above considered the effect of solvation on atomic species. Analogous experiments on clusters with molecular chromophores such as $I_2^-(Ar)_n$ and $I_2^-(CO_2)_n$ are also of interest, particularly in light of time-resolved experiments performed on these species by Lineberger and ourselves. By measuring high resolution photoelectron spectra of these clusters we determine the solvation energetics and learn about structural changes that occur upon solvation. Our studies on $I_2^-(Ar)_n$ (n=1-20) showed a decrease in slope in the stepwise solvation energy at n=6, indicating a weaker binding energy for the seventh (and higher) Ar atoms.[14] This is consistent with molecular dynamics simulations by Parson,[15] which predict that the first six Ar atoms form a ring around the I-I bond and can therefore interact with the partial negative charge on each I atom. Subsequent Ar atoms cluster can interact strongly with only a single I atom and therefore are not as strongly bound.

The photoelectron spectra also show that the I_2^- chromophore is vibrationally colder in $I_2^-(Ar)$ than in the bare I_2^- produced in our ion source. This can be understood because the binding energy of $I_2^-(Ar)$ is sufficiently small (53±4 meV)[14] so that clusters with four or more I_2^- vibrational quanta undergo predissociation before they can be photodetached. This reduction of vibrational complexity upon clustering with an Ar atom appears to be quite general and will be exploited in the proposed research program.

Our studies of $I_2^-(CO_2)_n$ are still in progress but have already revealed that the CO_2 solvent molecules are slightly bent in the anion clusters. This is evident from the observation of vibrational progressions in the CO_2 bend, just as we found previously for $X^-(CO_2)_n$ clusters. This result should be of considerable interest because all simulations of $X_2^-(CO_2)_n$ clusters performed to date[16-19] have assumed the CO_2 solvent molecules to be linear.

(c) Reactive intermediates and free radicals

We have characterized the ground and first excited states of the I_3 radical by photoelectron spectroscopy of I_3^- and $Ar{\cdot}I_3^-$ at 266 nm.[20] The electron affinity of I_3 is 4.226 ± 0.013 eV. Based on the recently determined bond dissociation energy of I_3^-,[21] the I_3 ground state is bound by 0.143 ± 0.06 eV, and the first excited state lies 0.27 eV above the ground state. The I_3 radical was proposed many years ago as an intermediate in the recombination of I atoms,[22-25] and our experiment represents the first determination that this species is thermodynamically stable. In addition, a vibrational progression is seen in the ground state band of the I_3^- photoelectron spectrum. The addition of an argon atom to I_3^- reduces the contribution of hot bands to the photoelectron spectrum, just as in the case of $Ar{\cdot}I_2^-$, facilitating the interpretation of the vibrational structure. Simulations indicate that the I_3 ground state is linear with a symmetric stretch frequency o 115 ± 5 cm^{-1} and is likely to be centrosymmetric.

The photoelectron spectra of the methoxide anions, CH_3O^- and CD_3O^-, were measured at considerably higher resolution[26] (8-10 meV) than in the only previously reported study (60 meV).[27] The spectra show resolved vibrational structure corresponding to vibrational levels of the CH_3O / CD_3O $\tilde{X}(^2E)$ state. These vibrational progressions are assigned to the degenerate ν_5 and ν_6 modes of the methoxy radical; no progressions in the totally symmetric stretch modes are observed. In addition, we obtain refined electron affinities: EA(CH_3O) = 1.568 ± 0.005 eV and EA(CD_3O) = 1.551 ± 0.005 eV.

We also obtained the photoelectron spectrum of the cyanonitrene anion, NCN^-, at 266 nm.[28] This spectrum reveals the $\tilde{a}\ ^1\Delta_g$ and the $\tilde{b}\ ^1\Sigma_g^+$ of NCN states together with the $\tilde{X}\ ^3\Sigma_g^-$ ground state for the first time. The low-lying singlet states are separated from the triplet ground state by 1.010 ± 0.010 and 1.629 ± 0.010 eV, respectively. We find a vibrational frequency of 1120 ± 50 c $^{-1}$ for the υ_1 mode of the $\tilde{b}\ ^1\Sigma_g^+$ state.

(d) Time-resolved studies of electron solvation dynamics in $I^-(H_2O)_n$ clusters

While much of our work on solvated halide anions has focused on frequency-domain photodetachment spectroscopy (part (a),above), we have also performed time-resolved experiments on electron solvation dynamics in $I^-\cdot(D_2O)_{n=4-6}$ and I^- $(H_2O)_{4-6}$ using femtosecond photoelectron spectroscopy (FPES). [29,30] In these experiments, an ultrafast pump pulse excites the anion to the cluster analog[31] of the charge-transfer-to-solvent state seen for I^- in aqueous solution. Evolution o this state is monitored by time-resolved photoelectron spectroscopy using an ultrafast probe pulse. We observe a profound change in the excited state dynamics as the number of water molecules increases. The excited n=4 clusters undergo simple population decay attributed to vibrational autodetachment.

However, in the n=5 and 6 clusters the solvent molecules rearrange to stabilize and localize the excess electron, showing characteristics associated with electron solvation dynamics in bulk water. Comparison of the FPES of $I^-(D_2O)_n$ with $I^-(H_2O)_n$ indicates more rapid solvation in the H_2O clusters.

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1. K. R. Asmis, T. R. Taylor, C. Xu and D. M. Neumark, "Anion Photoelectron Spectroscopy of I_2^- and $I_2^-Ar_n$ (n = 1 - 14, 16, 20) Clusters," J. Chem. Phys. 109, 4389, (1998).

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